

The effects of central metals on ammonia sensing of
metallophthalocyanines covalently bonded to graphene Oxide hybrids†
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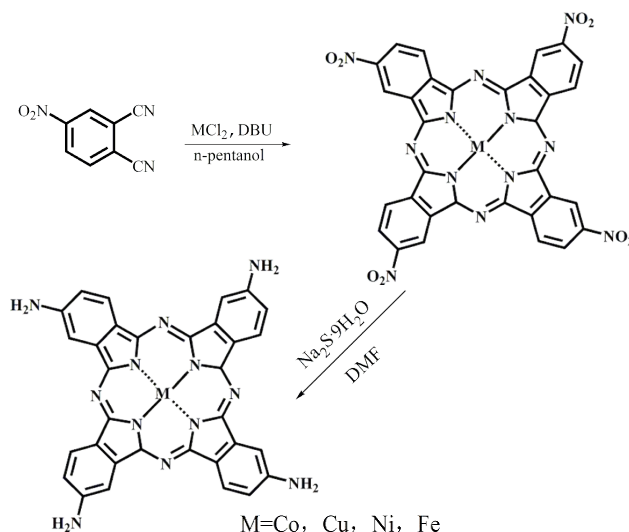
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1. Experimental detail

1.1 Materials

All chemicals were analytical grade and commercially available and used without further purification. 4-nitrophthalonitrile was purchased from Sigma-Aldrich Co. LLC., and was used without further purification. The synthesis scheme of tetra- β -aminephthalocyanines metal (II) (aPcMs M= Cu, Ni, Co, Fe) is shown in scheme S1.



Scheme S1. Synthesis scheme of tetra- β -aminephthalocyanines metal (aPcMs M= Co, Cu, Ni, Fe).

1.2 Characterization

EI and MALDI-TOF mass spectra were performed using an Agilent spectrometer (HP 5973N) and a Bruker microflex LT (Bruker Daltonics, Bremen, Germany) mass spectrometer, respectively. UV/Vis absorption spectra were recorded with a Lambda 35 UV/VIS spectrometer (Perkin-Elmer, USA). UV/Vis absorption spectra were recorded with a Lambda 35 UV/VIS spectrometer (Perkin-Elmer, USA). FT-IR spectra were recorded on a Nicolet FT-IR NEXUS spectrometer (Thermo Scientific).

1.3 Synthesis of tetra- β -aminephthalocyanine metal (aPcM)

Tetra- β -aminephthalocyanine metal (aPcMs M= Cu(II), Ni(II), Co(II), Fe(II)) were prepared by the same general method: 4-Nitrophthalonitrile (1.0g, 4.7 mmol) was dissolved in 10 ml of anhydrous n-pentanol with anhydrous metal dichloride (1.2 mmol) and 0.4 ml of 1,8-dicyanobicyclo- [5.4.0]-undec-7-ene (DBU). The solution was refluxed for 6h with continuous stirring under a N_2 atmosphere. The reaction mixture was cooled and product was precipitated in methanol solution. The precipitate was suction filtered and washed several times with the dilute hydrochloric acid and sodium hydroxide, and then washed with distilled water until the pH of the

supernatant approached 7. The rough product was washed several times with alcohol and then dried in a vacuum oven at 50 °C to obtained tetra-β-nitrophthalocyanine metal. Then, tetra-β-nitrophthalocyanine metal was dissolved in DMF with Sodium sulfide. The solution was heated up to 60°C for 2h. The precipitate was washed with ultrapure water until the pH of the supernatant approached 7, and then centrifugal washed with methanol until the centrifugal supernatant is colorless. The product was dried in a vacuum oven at 50 °C to obtained tetra-β-aminephthalocyanine metal.

Tetra-β-aminephthalocyanine Co (aPcCo): Electronic absorption spectrum (UV-Vis) in DMF: max (nm) = 714, 646. FT-IR spectra (KBr pellets) v: 3338, 3216, 1605, 1494, 1347, 830, 746 cm⁻¹. MALDI-TOF-MS (Fig S1A) Calcd (found): m/z = 631.31 (631.51) [M⁺].

Tetra-β-aminephthalocyanine Cu (aPcCu): Electronic absorption spectrum (UV-Vis) in DMF: max (nm) = 719, 645. FT-IR spectra (KBr pellets) v: 3319, 3203, 1599, 1496, 1385, 836, 746 cm⁻¹. MALDI-TOF-MS (Fig S1A) Calcd (found): m/z = 636.38 (636.13) [M⁺].

Tetra-β-aminephthalocyanine Ni (aPcNi): Electronic absorption spectrum (UV-Vis) in DMF: max (nm) = 720, 644. FT-IR spectra (KBr pellets) v: 3322, 3210, 1618, 1488, 1353, 799, 750 cm⁻¹. MALDI-TOF-MS (Fig S1C) Calcd (found): m/z = 631.18 (631.27) [M⁺].

Tetra-β-aminephthalocyanine Fe (aPcFe): Electronic absorption spectrum (UV-Vis) in DMF: max (nm) = 708, 675. FT-IR spectra (KBr pellets) v: 3359, 3197, 1611, 1462, 1322, 824, 746 cm⁻¹. MALDI-TOF-MS (Fig S1A) Calcd (found): m/z = 629.05 (629.13) [M⁺].

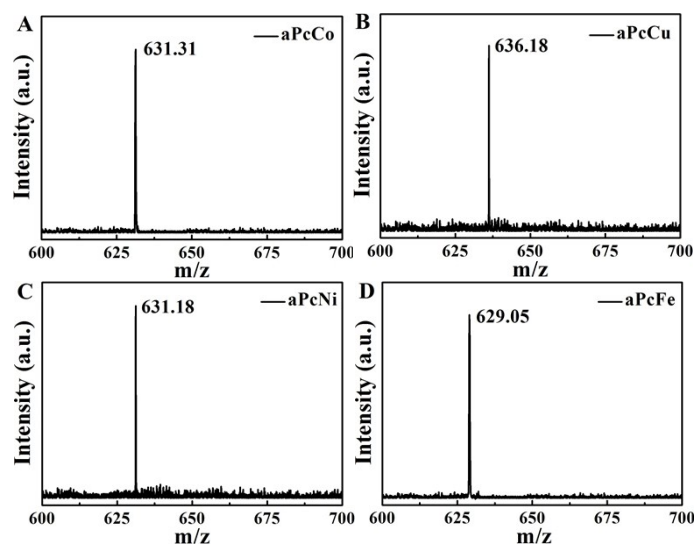


Fig. S1 MALDI-TOF mass spectra of (A) aPcCo-GO, (B) aPcCu-GO, (C) aPcNi-GO, (D) aPcFe-GO.

Result and discussion

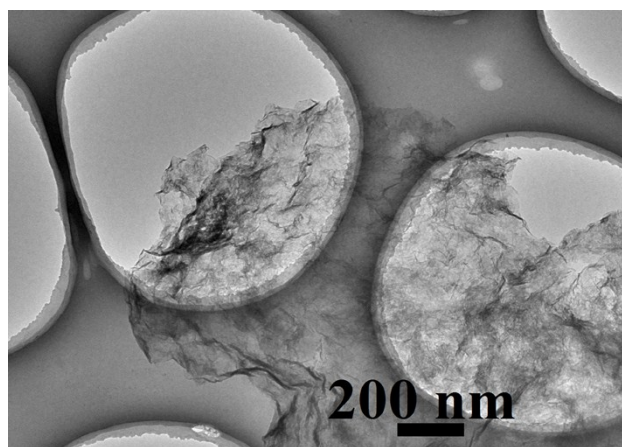


Fig. S2 TEM image of GO

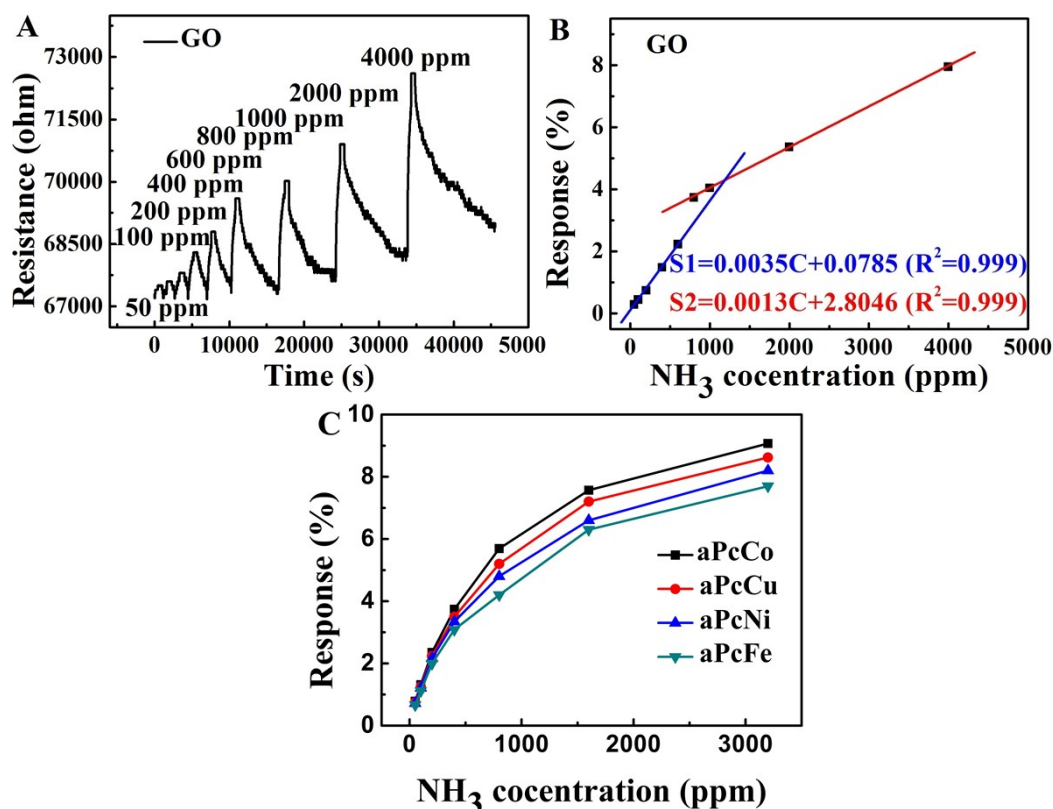


Fig. S3 (A) Resistance of GO sensor upon exposure to varying concentrations of NH₃; relationship of the response of (B) GO and (C) aPcM sensors to the concentration NH₃.

Table S1. Comparison of the detection performances of different NH₃ sensors

Sensor material	Response(%) / Detection conc. (ppm) ^[b]	Detection limit(ppm) ^[a]	Working temperature (°C) ^[c]	Response time(s) / Detection conc.(ppm) ^[b]	Recovery time (s) / Detection conc.(ppm) ^[b]	Detection range (ppm)	Ref.
CuO nanowires	3.1/100	10	200	360/100	1800/100	10-100	1
five-layer MoS ₂ sheets	~20/100	—	RT	~300/100	>600/100 (not fully)	100-1000	2

					recover)		
NiO nanowires	~30/100	—	400	~36/50	~600/50	50-200	3
Macroporous WO ₃	—	6.2	225	1200/74	~6000/74	6.2-74	4
Pt-WO ₃	2.7/2.5	0.62	225	~3600/5	~3600/5	0.62-5	5
Ag-doped - Fe ₂ O ₃ /SiO ₂	20/0.1	0.1	RT	125/4	380/4	0.1-100	6
Zn-doped NiO	40/50	5	RT	5/50	30/50	5-150	7
CeO ₂ @PANI	6.5/50	2	RT	57.6/50	300/50	2-400	8
PE-co-GMA nanofibers	2496/25	0.1	RT	75/1	600/25	0.1-25	9
PANI/Ag nanotubes	3/100	5	RT	~3000/100	~3000/100	5-100	10
RGO	5.5/200	200	RT	900	>1200/200(not fully recover)	200- 2800	11
Graphene	100/1000	0.5	RT	3600	3600		12
Phosphorus doped graphene nanosheets							13
SWCNTs on weighing paper	~1.5/5	0.36	RT	200/5	>900/5(not fully recover)	0.5-80	14
CNT-on-paper	~2.8/100	~5	RT	60/100	>4/100(not fully recover)	10-100	15
Au-coated CNT yarn	~2.0/50	0.5	RT	>300/50	2700/50	0.5-500	16
PANi@CNT	—	50	RT	~1200/50	—	50-5000	17

film							
MWCNTs/SnO ₂	12/10000	—	RT	~300/10000	unrecoverabl	—	18
/Ag	5/3.0				e		
aPcCo-GO	6.5/12.5	0.8	RT	340/3.0,12.5,	<350/50	0.8-	
	11.6/50			50		3200	
	2.6/6.0						
aPcCu-GO	3.5/12.5	0.8	RT	540/3.0,12.5,	<250/50	0.8-	This
	8.9/50			50		3200	wor
							k
aPcNi-GO	3.1/12.5	12.5	RT	580/12.5,50	845/50	12.5-	
	6.2/50					3200	
	2.6/200						
aPcFe-GO		50	RT	330/50,200	95/400	50-3200	
	6.1/800						

[a] If the sensor detection limit was not explicitly provided in the original report, then the lowest tested analyte concentration is listed.

[b] If the response (%), response time (s) or recovery time (s) of the sensor was not explicitly provided in the original report, then the estimate from the curve in that report is listed.

[c] RT, abbreviation for room temperature.

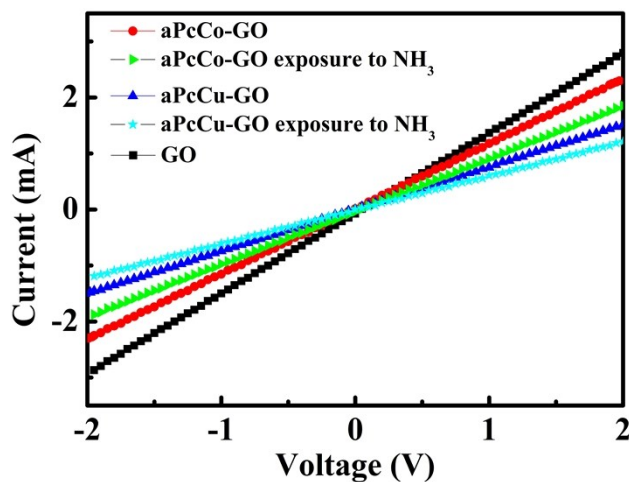


Fig. S4 I - V curves of the aPcM-GO and aPcM-GO exposure to NH_3 .

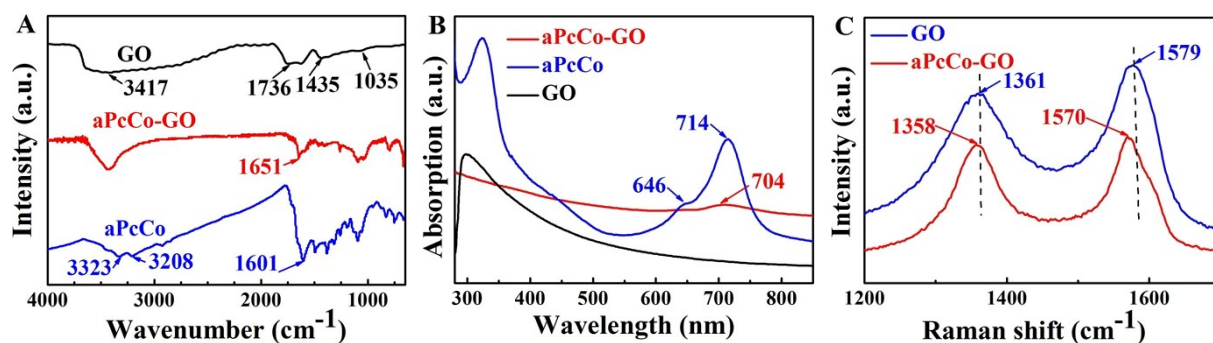


Fig. S5 (A) FT-IR spectra, (B) UV-Vis spectra and (C) Raman spectra of GO and aPcCo-GO hybrid obtained at $\lambda_{\text{exc}} = 457.9$ nm.

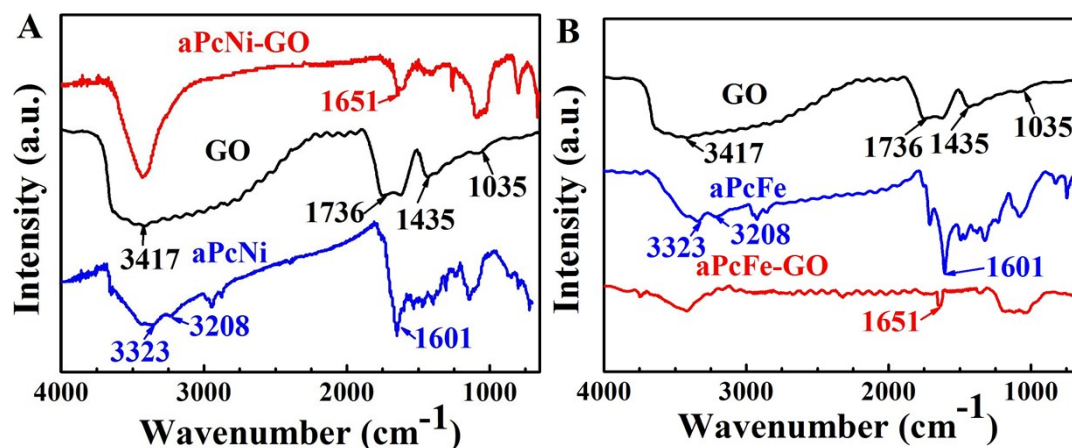


Fig. S6 FT-IR spectra of (A) GO, aPcNi and aPcNi-GO hybrid; (B) GO, aPcFe and aPcFe-GO hybrid.

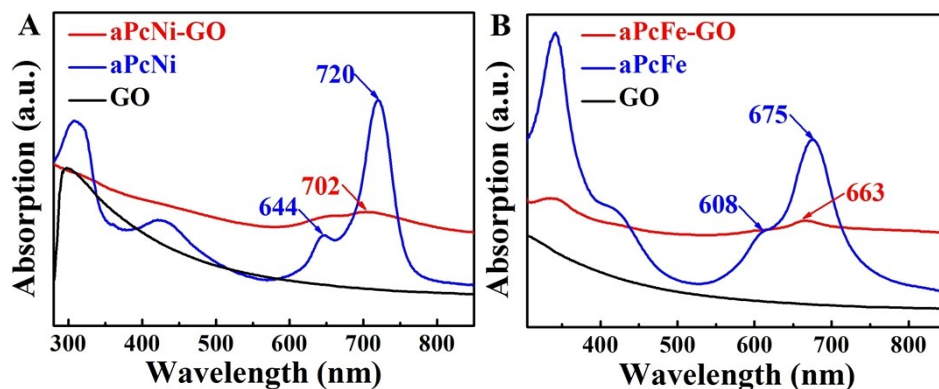


Fig. S7 UV-Vis spectra of (A) GO, aPcNi and aPcNi-GO hybrid; (B) GO, aPcFe and aPcFe-GO hybrid.

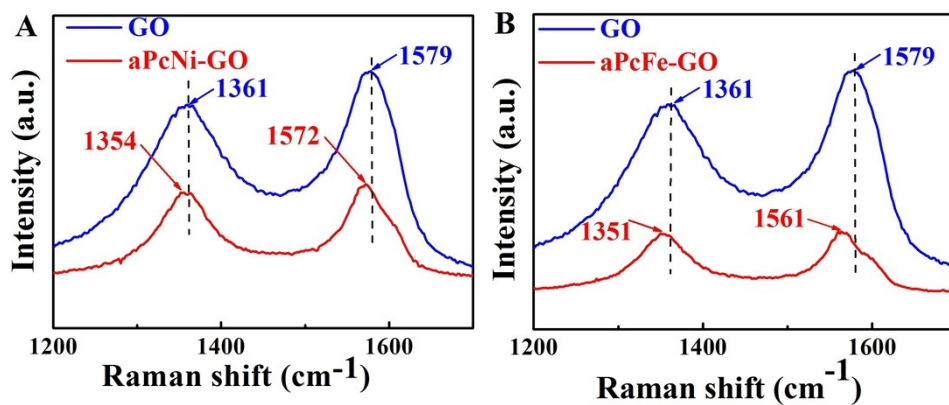


Fig. S8 Raman spectra of (A) GO, aPcNi and aPcNi-GO hybrid; (B) GO, aPcFe and aPcFe-GO hybrid.

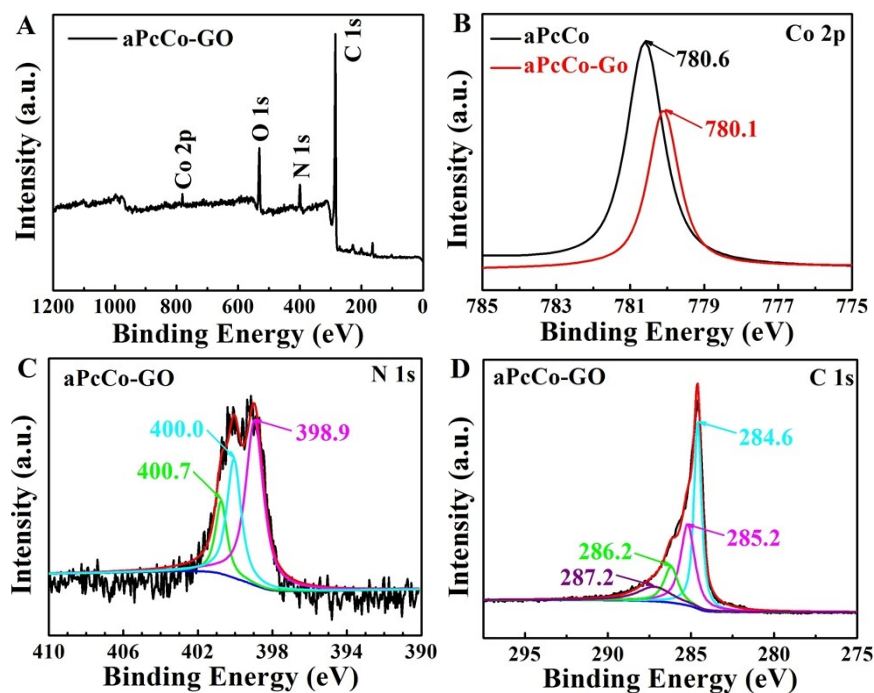


Fig. S9 XPS analysis of aPcCo-GO hybrids: (A) survey spectra; (B) N1s regions; (C) Co 2p region.

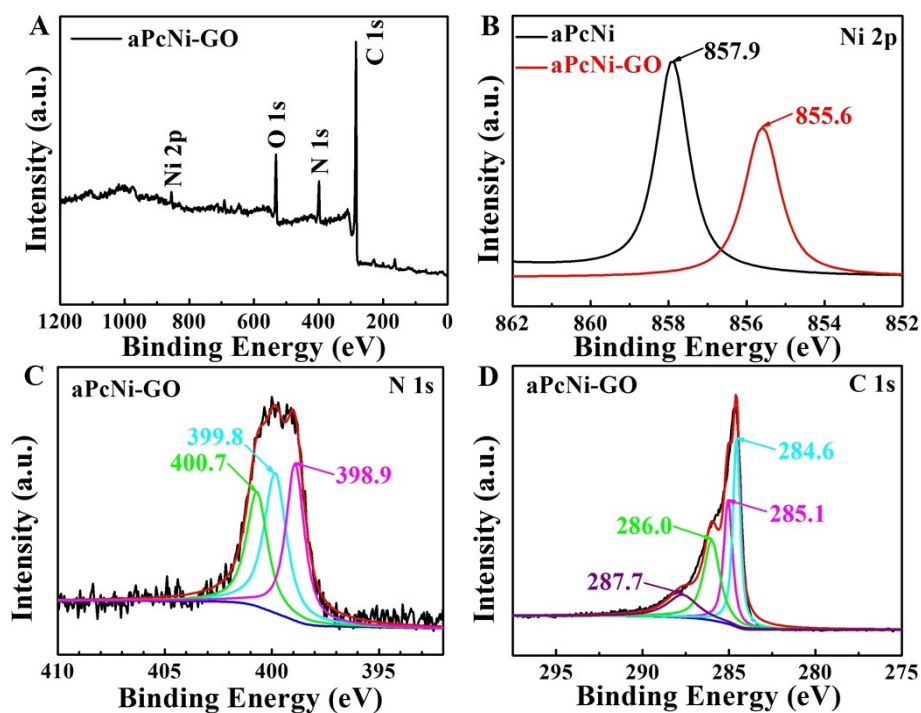


Fig. S10 XPS analysis of aPcNi-GO hybrids: (A) survey spectra; (B) N1s regions; (C) Ni 2p region

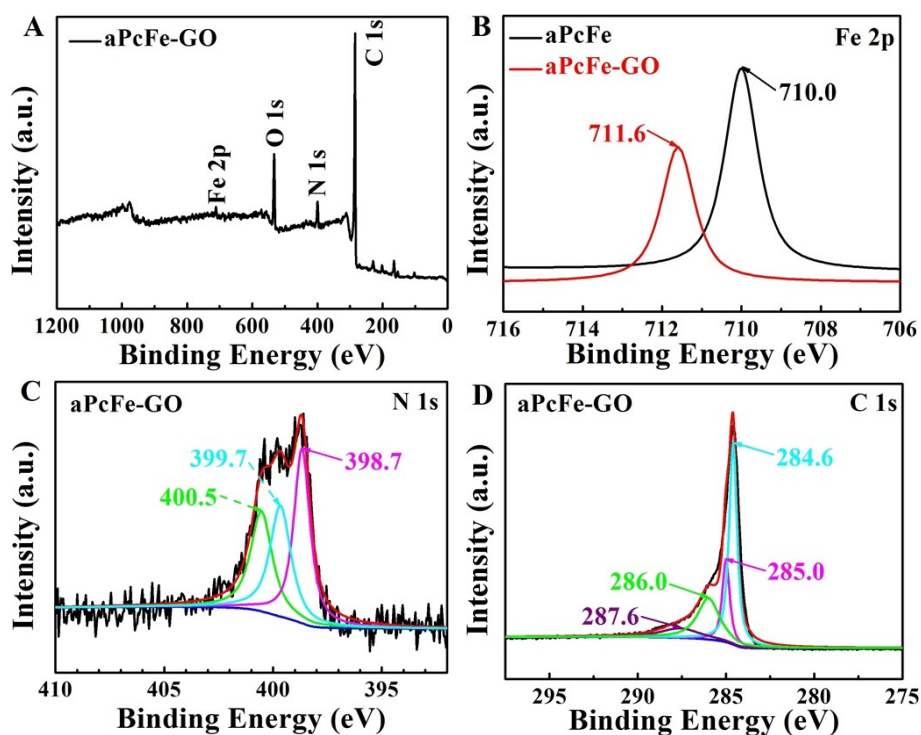


Fig. S11 XPS analysis of aPcFe-GO hybrids: (A) survey spectra; (B) N1s regions; (C) Fe 2p region

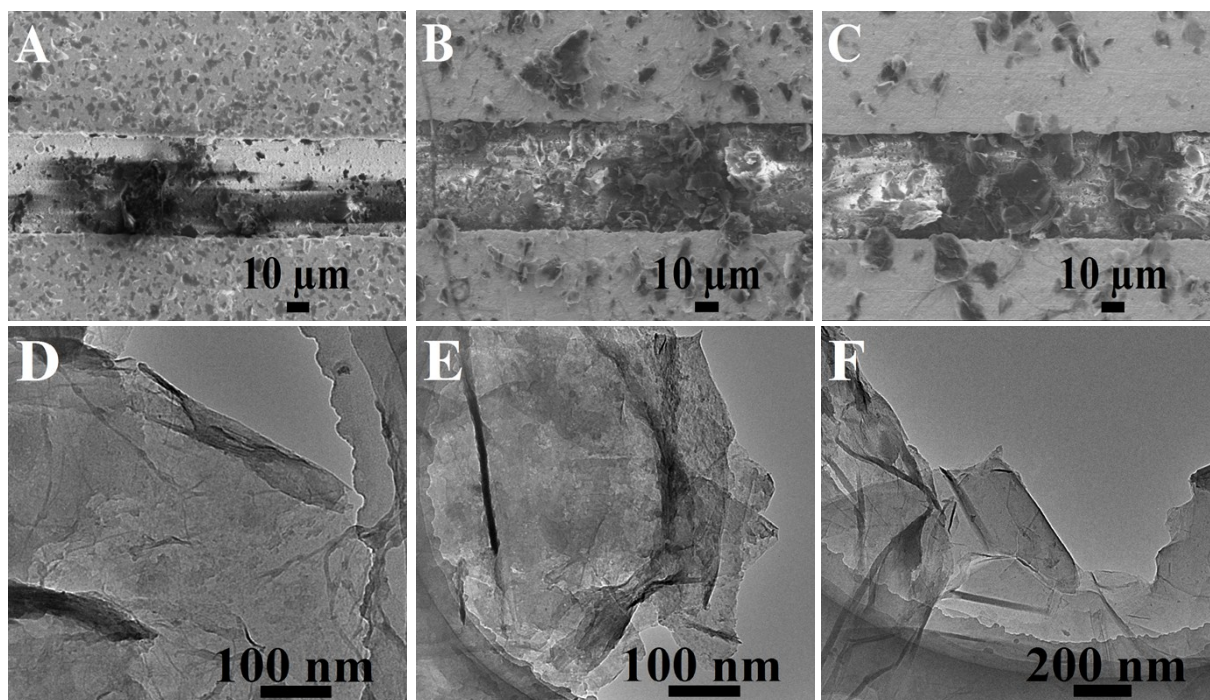


Fig. S12 (A-C) SEM and (D-F) TEM image of (A,D) aPcCo-GO, (B,E) aPcNi-GO and (C,F) aPcFe-GO.

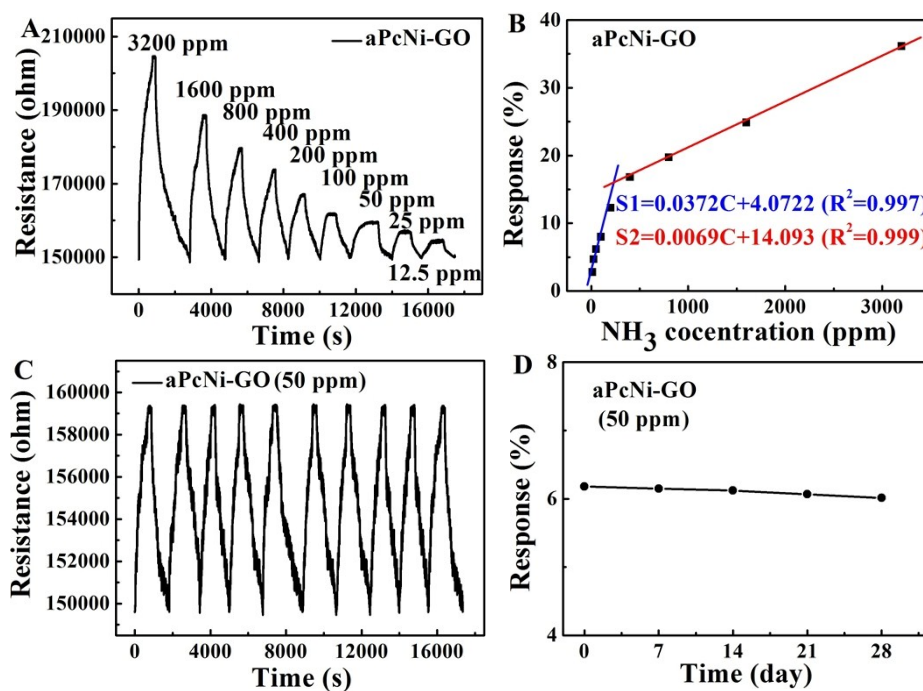


Fig. S13 (a) Response of aPcNi-GO hybrid sensor upon exposure to varying concentrations of NH₃; (b) relationship of the response of aPcNi-GO sensor to the concentration of NH₃; (c) ten sensing cycles of aPcNi-GO hybrid sensor to 50 ppm NH₃; (d) response of aPcNi-GO hybrid sensors to 50 ppm NH₃ over long time storage at 28°C.

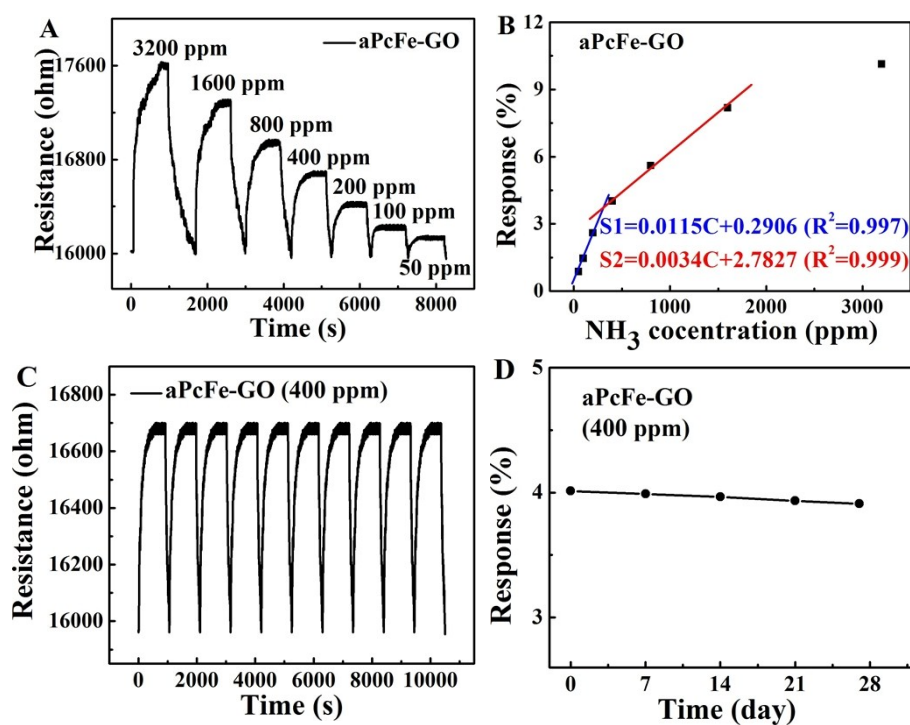


Fig. S14 (a) Response of aPcFe-GO hybrid sensor upon exposure to varying concentrations of NH_3 ; (b) relationship of the response of aPcFe-GO sensor to the concentration NH_3 ; (c) ten sensing cycles of aPcFe-GO hybrid sensor to 400 ppm NH_3 ; (d) response of aPcFe-GO hybrid sensors to 400 ppm NH_3 over long time storage at 28°C .

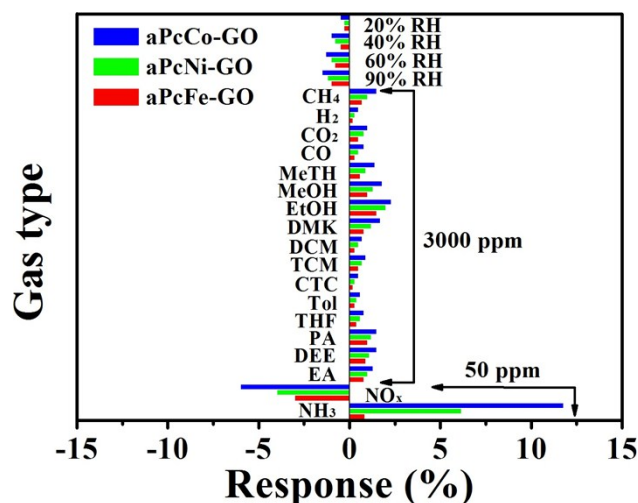


Fig. S15 Cross-sensitivities to various gases for the aPcM-GO sensors at 28°C , MeTH = methanal, MeOH = methanol, EtOH = ethanol, DMK = acetone, DCM = dichloromethane, TCM = trichloromethane, CTC = carbon tetrachloride, Tol = toluene, THF = tetrahydrofuran, PA = propionic acid, DEE = diethyl ether, EA = ethyl acetate.

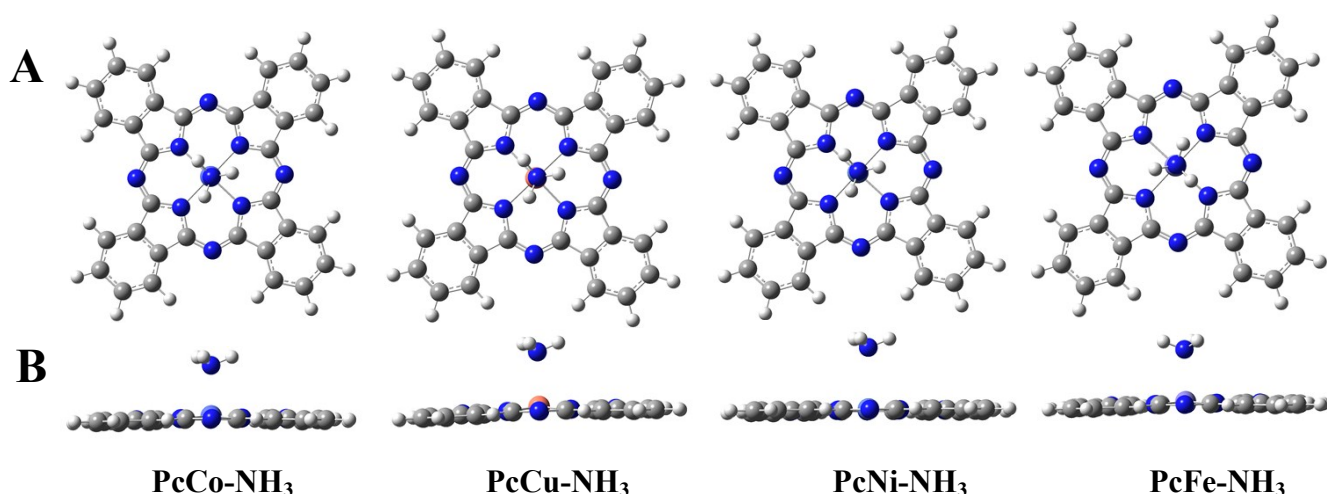


Fig. S16. Optimized structures of NH₃-aPcMs with (A) top and (B) side views.

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